

IV.B.7 Development of a Low-Cost, Durable Membrane and Membrane Electrode Assembly for Stationary and Mobile Fuel Cell Application

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Objectives

- Develop a low-cost, durable membrane.
- Develop a low-cost, durable membrane electrode assembly (MEA).
- Validate the MEA performance in single cells and in stacks.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Materials and Manufacturing Costs
- P. Durability

Approach

- Develop new material for membranes based on polyvinylidene fluoride (PVDF)/polyelectrolyte blends.
- Develop a process to make fuel cell membranes from these materials.
- Develop MEAs based on these novel membranes.

Accomplishments

- Prepared a library of sulfonated polyelectrolytes.
- Developed a laboratory process to blend PVDF with the polyelectrolyte.
- Developed a laboratory and pilot plant process to prepare membranes from these materials.
- Developed a process to activate the membranes.
- Prepared MEAs that exhibit equal or better polarization curves than those made from commercial perfluorosulfonated ionomers at 100% relative humidity.
- Achieved 2100 hours durability in a fuel cell.

Future Directions

- Complete high-throughput equipment to prepare and test libraries of polyelectrolytes.
 - Optimize polyelectrolyte architecture and composition for conductivity, low relative humidity, and durability.
 - Scale up most promising candidates.
 - Optimize PVDF/polyelectrolyte blending process.
 - Develop a pilot process for membrane activation.
 - Optimize MEA construction and assembly process for PVDF-based membrane.
 - Investigate MEA failure mechanism.
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Introduction

Proton exchange membrane (PEM) fuel cells rely on perfluorosulfonated acids (PFSA) for the construction of the membranes. The cost of these materials is high due largely to complexity and the number of steps involved in their synthesis. In addition, they suffer other shortcomings such as mediocre mechanical properties and insufficient durability for some applications.

Approach

The team, lead by Atofina, is examining the feasibility of using other materials for the membrane based on polyvinylidene fluoride (PVDF)/ polyelectrolyte blends. PVDF exhibits an exceptional combination of mechanical, chemical, and electrochemical properties. For example, Kynar® (Atofina's trade name for PVDF) is used in the chemical industry in very difficult environments such as contact with hydrochloric (HCl) and hydrofluorhydric (HF) acids. It is also extensively used in lithium ion batteries, where PVDF "sees" a potential up to 4.2 V. These novel materials offer potentially a much lower cost than PFSA (at equal production volume) because their preparation process is much simpler. However, because they are new and different from PFSA, each step must be revisited and optimized. This is particularly true for the composition of the MEA and its preparation process. Indeed, nearly all MEAs used in prototypes today rely on PFSA, and years of optimization went into their fabrication.

Results

The first task at hand is to prepare polyelectrolyte candidates of various architecture, composition, molecular weight, polydispersity, etc. Many such polymers have been prepared and, after blending with Kynar®, were processed to make membranes. The blending process of the PVDF with the polyelectrolyte is now nearly optimized and is very reproducible on a laboratory scale. Several classical polymer film processes such as extrusion, water borne casting (from latex) and solvent casting have been studied. The process has been taken several times to a pilot plant level and its excellent reproducibility demonstrated. Most of the trials were carried out to produce membrane in the 17 to 50 μm range. Quality control demonstrated that the membrane quality is very high throughout. The activation step (acidification + rinsing) has been considerably optimized at the laboratory scale. Specialized equipment will be needed for pilot scale-up. This equipment has been designed, and quotes have been obtained for its construction.

The membranes have been fully characterized in ex-situ testing. Mechanical properties are very good. Permeability to hydrogen is about one third that of PFSA. Conductivity is about 60% of that of PFSA in water at 70°C, or about 130 mS/cm. While the conductivity is not as high as that of PFSA, due to the fact that both mechanical properties and the gas permeability are excellent, it is possible to make thin membranes that exhibit excellent area resistance.

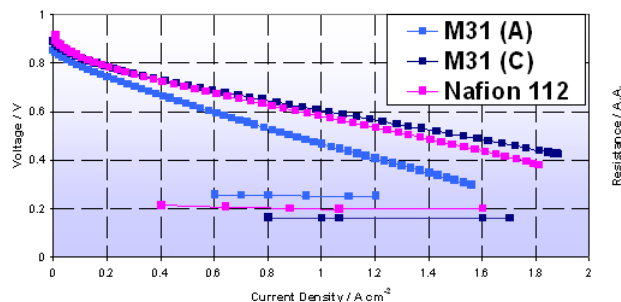


Figure 1. Optimization of MEA Construction Leads to Polarization Curve Similar to that Obtained with Nafion[®]112

We prepared MEAs by laminating membranes with commercial electrodes from E-TEK. It became apparent very early that specific optimization of the MEA composition and process is required and that existing procedures applied to commercial PFSA's do not work well with the Atofina membranes. Figure 1 illustrates this point clearly. Transposing a typical recipe used for Nafion[®]112 does not yield good performance. However, after optimization, it is possible to match the polarization curve of Nafion[®]112 [60°C, 100% relative humidity (RH), oxygen].

Initial work was carried out using oxygen. Switching to air also required a specific MEA optimization, as illustrated in Figure 2.

While working well at high RH, the conductivity drops sharply at lower RH, and water management problems are observed with our E-TEK electrode-based MEAs. Johnson Matthey is currently working on this important issue.

A 2100-hour endurance test has been conducted (60°C, 100% RH, oxygen, 550 mA/cm²). Significant progress has been achieved in terms of decay rates. Previous tests with the same membrane showed a decay rate of 175 μ V/h, then 80 μ V/h, and now 45 μ V/h. This is still an order of magnitude over existing commercial materials. However, it is noteworthy that these improvements in decay rates have been achieved only by manipulating the MEA process since the same membrane was used. Membrane thinning was observed in some areas, and the failure mechanism is now under investigation.

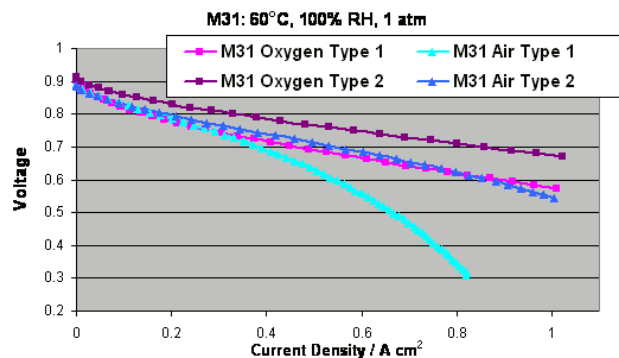


Figure 2. Optimization of MEA Construction Leads to Satisfactory Performance in Air

Conclusions

A new membrane is being developed by Atofina based on novel PVDF/sulfonated polyelectrolyte blends. Procedures have been developed for each step of the fabrication process. Due to the low cost of the starting materials and the simplicity of the manufacturing process, the Atofina membrane should be less expensive than commercially available PFSA-based membranes. The membrane features excellent mechanical properties and impermeability to hydrogen as well as satisfactory proton conductivity. Provided that the composition and manufacturing process of the MEA is adapted for the PVDF-based membrane, good polarization curves are obtained under oxygen or air at 60°C and 100% relative humidity. We showed that the durability is greatly impacted by the quality of the MEA using otherwise the same membrane. However, at this early stage, the decay rate is still one order of magnitude too high: 45 μ V/h over 2100-hour period.

Future work will focus on the improvement of the polyelectrolyte and of the membrane, particularly using high-throughput techniques. The preparation of the promising candidates with respect to improved proton conductivity and durability will be scaled up. We will also continue to work on the membrane manufacturing and scale up the activation process. Johnson Matthey will address the MEA composition and manufacturing process, as both need to be optimized for the Atofina membrane. We will also investigate the degradation mechanism on a high-priority basis. UTC Fuel Cells will become more involved in the validation when suitable MEAs become available.

FY 2004 Publications/Presentations

1. Project Kick-off Meeting Presentation –
February 17, 2004, Washington, DC
2. First Quarterly Review Meeting Presentation –
March 19, 2004, Washington, DC
3. Presentation at the DOE Hydrogen Program
Review – May 25, 2004, Philadelphia, PA